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Closed Loop System for the Treatment of Waste Pickle Liquor

Crown Chemical Co, Inc, Indianapolis, Ind

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

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16. ABSTRACT: The report gives results of a demonstration of the feasibility of converting ferrous sulfate ($FeSO_4 \cdot 7H_2O$)--obtained by low-temperature crystallization from H_2SO_4 waste pickle liquor generated by the acid-cleaning of steel surfaces--to marketable ferric oxide (Fe_2O_3). A closed-loop system is proposed, consisting of a crystallizer, ion exchange unit, oxidizer, and hydrolyser. All acids are recycled, and the net effect is that $FeSO_4 \cdot 7H_2O$ is consumed and Fe_2O_3 is produced. The $FeSO_4 \cdot 7H_2O$ solution was contacted with hydrogen ion exchange resin in a continuous ion exchange unit. Removal of ferrous ion was 90%. About 11-15% by weight H_2SO_4 was generated for recycle to pickling. The resin was regenerated with 4M HNO_3, and a ferrous-ferric nitrate solution was produced. This product was heated to 180 C and contacted with air to get complete oxidation to the ferric state and to oxidize any by-product NO_2 to HNO_3. The nitrate solution was then hydrolysed to Fe_2O_3 and HNO_3 in a continuous coil autoclave at 205 C. The HNO_3 was about 20% by weight and can be recycled to the ion exchange unit. After drying, the Fe_2O_3 was about 99% pure. A preliminary market survey indicates the product may have a value of $0.10-$0.80 per kilogram.

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Sulfuric Acid	Ferric Oxide	07B
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CLOSED LOOP SYSTEM FOR THE TREATMENT OF WASTE PICKLE LIQUOR

by

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TABLE OF CONTENTS

		Page
Figures		iv
Tables		v
Acknowledgments		vi
Section		
1	Introduction	1
2	Conclusions	4
3	Recommendations	5
4	Proposed Process Summary	6
5	Proposed Process Description	8
	5.1 Acid Recovery System and Ferrous Sulfate Heptahydrate Production	8
	5.2 Ion Exchange	12
	5.2.1 Introduction	12
	5.2.2 Proposed Production Plant	13
	5.2.3 Flow Rates in the Ion Exchange Unit	17
	5.2.4 Operation of the Unit	17
	5.3 Oxidation Unit	19
	5.4 Hydrolysis (see Experimental Work)	19
	5.5 Solid-Liquid Separation	19
	5.6 Drying	19
	5.7 Plant Costs	19
6	Experimental Work	23
	6.1 Ion Exchange	23
	6.1.1 Operation of Unit and Sampling	23
	6.1.2 Loading Conditions and Preparation of Sulfuric Acid	27
	6.1.3 Stripping Conditions	31
	6.1.4 Resin Capacity and Stability	39
	6.2 Oxidation Tower	40
	6.3 Hydrolysis	40
7	Analytical Methods	46
8	Preliminary Market Analysis	47
	8.1 Introduction	47
	8.2 Iron Oxide Pigment Sales	48
	8.3 Technology	61
9	References	64

LIST OF FIGURES

Number		Page
1	Distribution of steel finishing plants	8
2	Proposed process schematic	7
3	Schematic of low temperature crystallizer	9
4	Solubility of ferrous sulfate in various sulfuric acid concentrations	11
5	Schematic of double loop contactor resin: Dowex HGR-W, 500 cu. ft. (14.16 cu m)	14
6A	Schematic of pilot plant contactor operated for concentrated nitrate product	15
6B	Schematic of pilot plant contactor resin: operated for concentrated H_2SO_4	16
7	H_2SO_4 - normality versus percent by weight	28
8	Loading profile code: 30-34	29
9	Loading profile code: 35-38	30
10	Loading profile code: 59-62	32
11	Loading profile code: 63-65	33
12	Degree of stripping relative to excess nitric acid	34
13	Strip profile code: 7-12	35
14	Strip profile code: 52-55	36
15	Strip profile code: 56-58	37
16	Laboratory hydrolyzer 300 ml capacity	42
17	Continuous coil hydrolyzer	44

LIST OF TABLES

Number		Page
1	Solubility of Ferrous Sulfate Heptahydrate in Sulfuric Acid Solutions	10
2	Capital and Operating Costs of Full-Scale Crown Acid Recovery System, Ion Exchange System, and Hydrolyser to Produce Ferric Oxide	20
3	Capital and Operating Costs (Ion Exchange Only)	21
4	Daily Average Flow Rates - ml/min	24
5	Daily Average Analysis of Inlet Streams	25
6	Daily Average Analysis - Exit Streams	25
7	Iron on Stripped Resin	38
8	Nitrate Material Balance Before and After Use of Oxidation Recovery Tower	41
9	Final Continucus Hydrolyzer Test Report	46
10	Finished Iron Oxide Pigments Sold by Processors in the United States, By Kind	49
11	Salient Iron Oxide Pigments Statistics in the the United States	50
12	Producers of Iron Oxide Pigments in the United States in 1975	52

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SECTION 1

INTRODUCTION

The problem of the disposal of spent pickle liquor (acid plus iron salts) is widespread throughout the metalworking industry. It results from a great percentage of metal-surface-cleaning treatments. Operations such as cold rolling, wire drawing, galvanizing, tin-plating, and extrusion are among these. Figure 1 shows the geogrsphical distribution of metalworking plants with 20 or more employees which normally use acid pickling as a surface-cleaning method. A recent EPA publication [1] estimates well in excess of 100 major pickling locations.

The disposal of effluent from these plants poses a serious problem in maintaining the water quality in plant areas. Current methods for the disposal of pickle liquor include neutralization, pumping into deep wells, removal to remote land areas, and deep sea disposal. All of these methods cause change in the surrounding environment.

Recently, attempts have been made to develop sophisticated acid recovery systems to enable metalworking firms to recover some waste acid and alleviate the pollution problem.

Systems currently exist and are in operation to regenerate HCl by roasting. Reports indicate that these and other "noncatalyst-using" systems consume excessive energy and are high in capital cost.

There also exist systems for removal of ferrous sulfate from sulfuric acid pickle liquors by low temperature crystallization. One such system is described in the Process Description section of this report. This system is relatively low in cost and energy requirements.

However, in many areas of the country ferrous sulfate is in oversupply and is not a salable product. Its possible disposal as landfill is questionable.

The process described in this report is a closed loop system in which:

1) Sulfuric acid is returned to the pickling process,

2) Marketable ferric oxide is produced.

The process offers the possibility of converting pollution control from a nonproductive expense to a lower cost or, perhaps, a profitable operation.

The objective of this project was to explore the technical and economic feasibility of the process.

The two most important technologies needing investigation were:

1) Ion Exchange,

2) Hydrolysis.

Therefore, experimental work was mainly limited to these two unit operations.

SECTION 9

CONCLUSIONS

The work reported establishes the feasibility of an ion exchange-hydrolysis system to produce Fe_2O_3 from $FeSO_4 \cdot 7H_2O$.

The proposed crystallization, ion exchange, oxidation, hydrolysis process offers a complete recycle treatment for the treatment of waste pickle liquor. It also offers the possibility of relieving a serious environmental pollution control problem. The production of probably marketable ferric oxide, offsetting the cost of waste treatment, is an attractive feature. However, a firm value for the product has not been established. It probably lies in the range of $0.10-$0.80 per kilogram.

Other technologies in the steel industry are beginning to produce an iron oxide product. The affect of these products on the future market has not been assessed.

The fact that the ion exchange and the hydrolyzer work were carried out in separate locations is not of as great importance as might appear at first glance since they are quite separate unit operations.

A more serious problem is that a double loop ion exchanger has not been built, although there is no reason it would not operate as proposed.

Some plugging problems occurred with the continuous coil hydrolyzer. Occasionally, nitrogen dioxide was observed.

SECTION 3

RECOMMENDATIONS

It is recommended that:

1) Further pilot scale hydrolysis work be done with the objective of continuous production of ferric oxide to determine baseline data on production rates and costs.
2) A pilot plant be built with a double loop ion exchange unit and a hydrolyzer operating continuously on the same level.
3) An engineering analysis be made to establish specifications for all units including auxiliary equipment such as oxidation towers, scrubbers, pressure letdown vessels, centrifuging equipment, dryer, pumps, piping, instruments, product storage, and bagging.
4) A combined market research, technology assessment be made. The objectives would be to establish the market value of the typical ferric oxide product, establish the market value of products from reported competing technologies for waste pickle liquor treatment, evaluate comparative process economics and assess the impact on the market of emerging new products, and recommend the best system to industry.
5) A demonstration plant be considered.

SECTION 4

PROPOSED PROCESS SUMMARY

The initial step is a low-temperature crystallization of ferrous sulfate heptahydrate from waste sulfuric acid pickling liquid. The recovered sulfuric acid is recycled to the pickling process.

The ferrous sulfate heptahydrate is redissolved and introduced into an ion exchange column and contacted with a cationic exchange resin. Ferrous ions are absorbed on the resin and hydrogen ions are released to yield approximately 18 percent by weight H_2SO_4 for recycling to the pickling process. The resin is then regenerated with concentrated nitric acid, and a solution of iron nitrate is produced.

The nitrate solution containing ferrous and ferric ions, excess nitric acid, and some byproduct nitrogen dioxide are passed through an oxidizing tower to oxidize the NO_2 back to nitric acid and complete the conversion to ferric ion.

The resulting ferric nitrate, nitric acid solution is then passed through a continuous coil hydrolyzer at about 205°C to convert the ferric nitrate to ferric oxide. The solid ferric oxide is separated from the nitric acid solution and dried. The recovered nitric acid is recycled to the ion exchange column.

A schematic of the proposed plant is shown in Figure 2.

Since the patent literature has not been searched, the present patent situation is unknown. The patentability of the process using double loop ion exchange combined with the continuous coil hydrolyzer should be determined.

SECTION 5

PROPOSED PROCESS DESCRIPTION

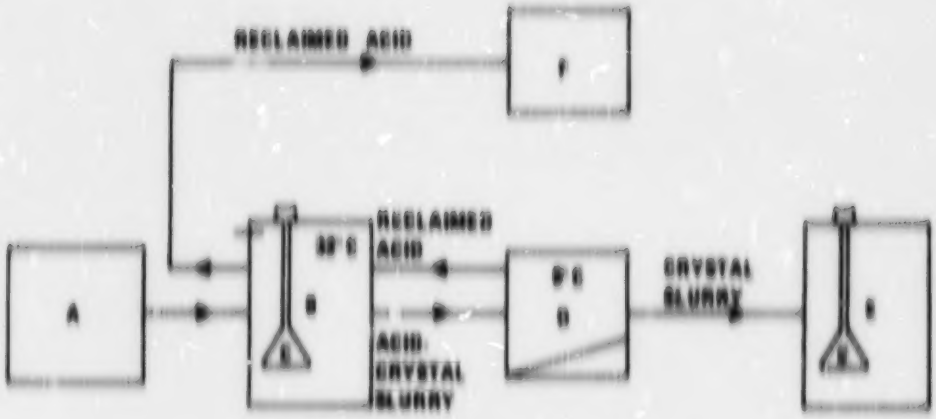
5.1 ACID RECOVERY SYSTEM AND FERROUS SULFATE HEPTAHYDRATE PRODUCTION

Acid recovery systems for waste pickle liquors are commercially available. One such is the system marketed by Crown Environmental Control Systems, Inc., a Division of Crown Chemical Co., Inc., of Indianapolis, Indiana. The Crown plant at the LaClede Steel Company in Alton, Illinois, recovers approximately 76,000 liters (20,000 gallons) per day of spent pickle liquor and produces 7.26 million kg (8,000 tons) per year of ferrous sulfate heptahydrate. A schematic plant diagram is shown in Figure 3. The process is based on the decreasing solubility of the ferrous sulfate with decreasing temperature (see Table 1 and Figure 4).

Waste acid is pumped from the Pickling Tank or the Storage Tank to the Treating Tank and cooled to 32°C with agitation. The material from the Treating Tank is then pumped to the Settling Tank. There the material is further cooled to approximately 0°C. After cooling, reclaimed acid is pumped back to the Treatment Tank and then to a Storage Tank. The crystal slurry is pumped from the settling tank to the crystal storage tank and from there to the tank car for shipment.

Total operating and maintenance costs based on 300 days per year of operations are:

System Batch Size	8 Hr./Day	24 Hr./Day
38,000 liters (10,000 gallons)	$11,150	$23,500
28,500 liters (7,500 gallons)	$ 8,500	$17,900
19,000 liters (5,000 gallons)	$ 7,000	$14,000
13,300 liters (3,500 gallons)	$ 6,000	$11,800



A : WASTE ACID STORAGE TANK
B : TREATMENT TANK
C : AGITATOR
D : SETTLING TANK
E : CRYSTAL STORAGE TANK
F : STORAGE TANK

FIGURE 3. SCHEMATIC OF LOW TEMPERATURE CRYSTALLIZER

TABLE 1. SOLUBILITY OF FERROUS SULFATE HEPTAHYDRATE IN SULFURIC ACID SOLUTIONS

H_2SO_4	$FeSO_4$ SW/W*		
SW/W*	32°C	25°C	45°C
2.5	12.66	21.31	29.34
5	11.62	19.77	27.70
7.5	10.61	18.41	26.37
10	9.61	17.30	25.52
12.5	8.63	17.15	24.66
15	7.70	15.06	23.22
20	6.09	13.17	
25	4.46	11.41	
30	3.21	10.29	
35	2.91	8.51	
40	2.69		
45	2.64		

*weight/total weight.

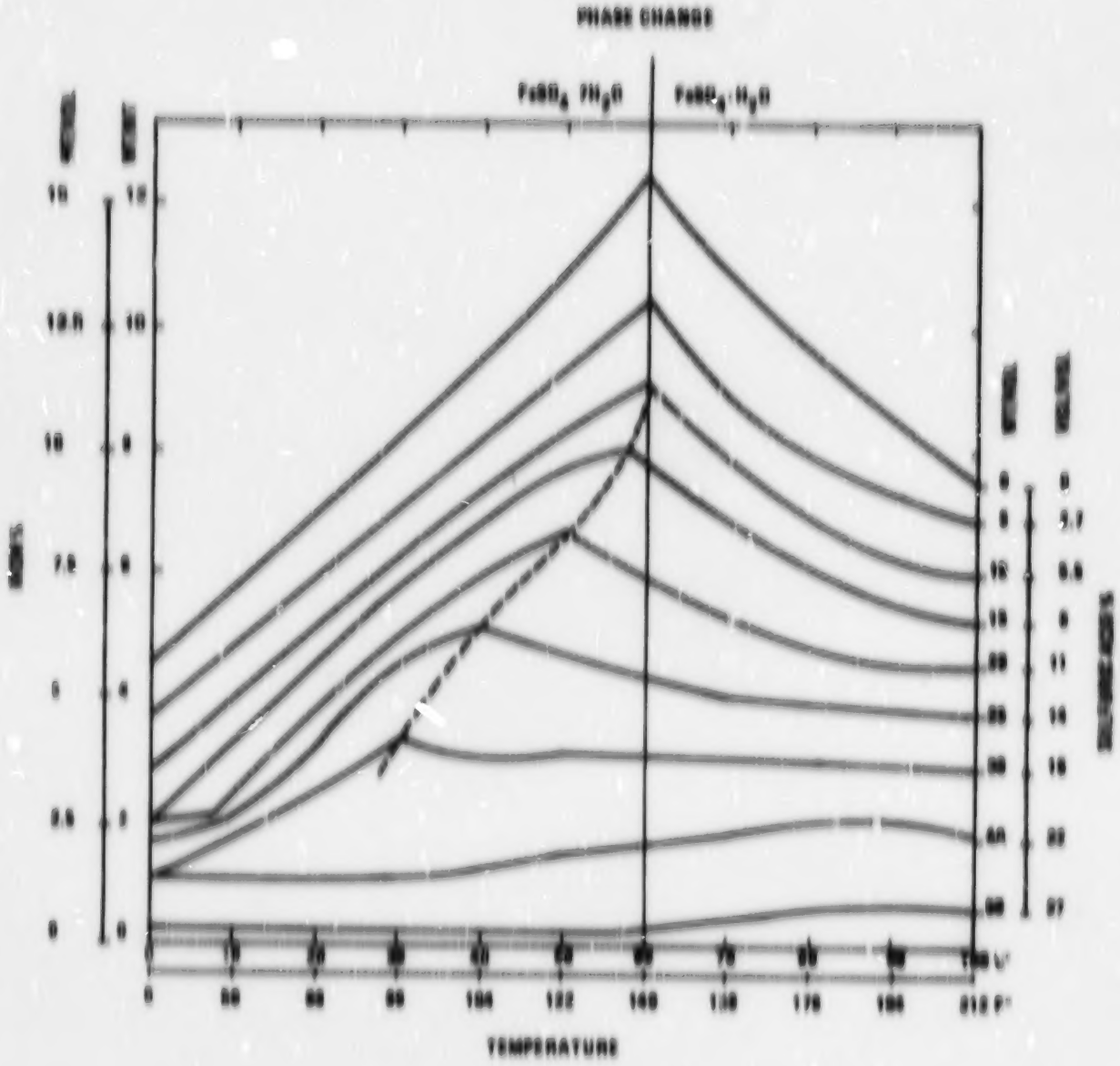


FIGURE 4. SOLUBILITY OF FERROUS SULFATE IN VARIOUS SULFURIC ACID CONCENTRATIONS

An average analysis of the recovered ferrous sulfate crystals is:

$FeSO_4 \cdot 7H_2O$	99.6%
Sulfate	33.0%
Water	45.5%
Iron (Fe^{++})	21.0%
Copper	0.005%
Lead	0.03%
Manganese	0.01%
Tin	0.001%
Zinc	0.01%
Silicon	0.001%
pH (of Slurry)	1.2

Since such commercial systems for ferrous sulfate crystals exist, no experimental work was done. Commercial crystals were used as feed.

5.2 ION EXCHANGE

5.2.1 Introduction

The proposed ion exchange process is based on a study made by the Chemical Separations Corporation, Oak Ridge, Tennessee, for the U. S. Federal Water Pollution Control Administration [2]. A number of pertinent patents were issued to I. R. Higgins as a result, including these:

U. S. Patent 3,470,022, Process and Apparatus for Process Pickling Liquor, and

U. S. Patent 3,468,707, Hydrolyser Process for Steel Pickling Liquors.

It is reported that the double loop ion exchange process proposed herein is covered by U. S. Patent 3,677,937 [3].

The process chemistry may be represented by the following equations:

a. Ion Exchange Loading

$$FeSO_4 + 2H\text{-}R \rightleftharpoons Fe\leq^{R}_{R} + H_2SO_4$$

b. Ion Exchange Regeneration

$$Fe\leq^{R}_{R} + 2HNO_3 \rightleftharpoons 2\ H\text{-}R + Fe(NO_3)_2$$

c. Oxidation from Ferrous to Ferric ion

$$Fe^{++} + 2H^{+} + NO_3^{-} \rightarrow Fe^{+++} + NO_2 + H_2O$$

d. Nitrogen Dioxide Oxidation (in oxidation unit)

$$2NO_2 + H_2O + 1/2\ O_2 \rightarrow 2HNO_3$$

5.2.2 Proposed Production Plant

The use of double loop countercurrent flow is well suited to the process in which the concentration of both the sulfuric acid and ferrous nitrate products must be maximized and tons of products per day are to be produced.

It is proposed to build a double loop countercurrent ion exchange contactor designed for the production of 5,442 kg (6 tons) per day of ferric oxide. A schematic drawing of the unit is shown in Figure 5. However, it should be noted that all of the experimental work in this study was carried out in a single loop contactor such as shown in Figures 6A and 6B. No commercial double loop unit exists at present.

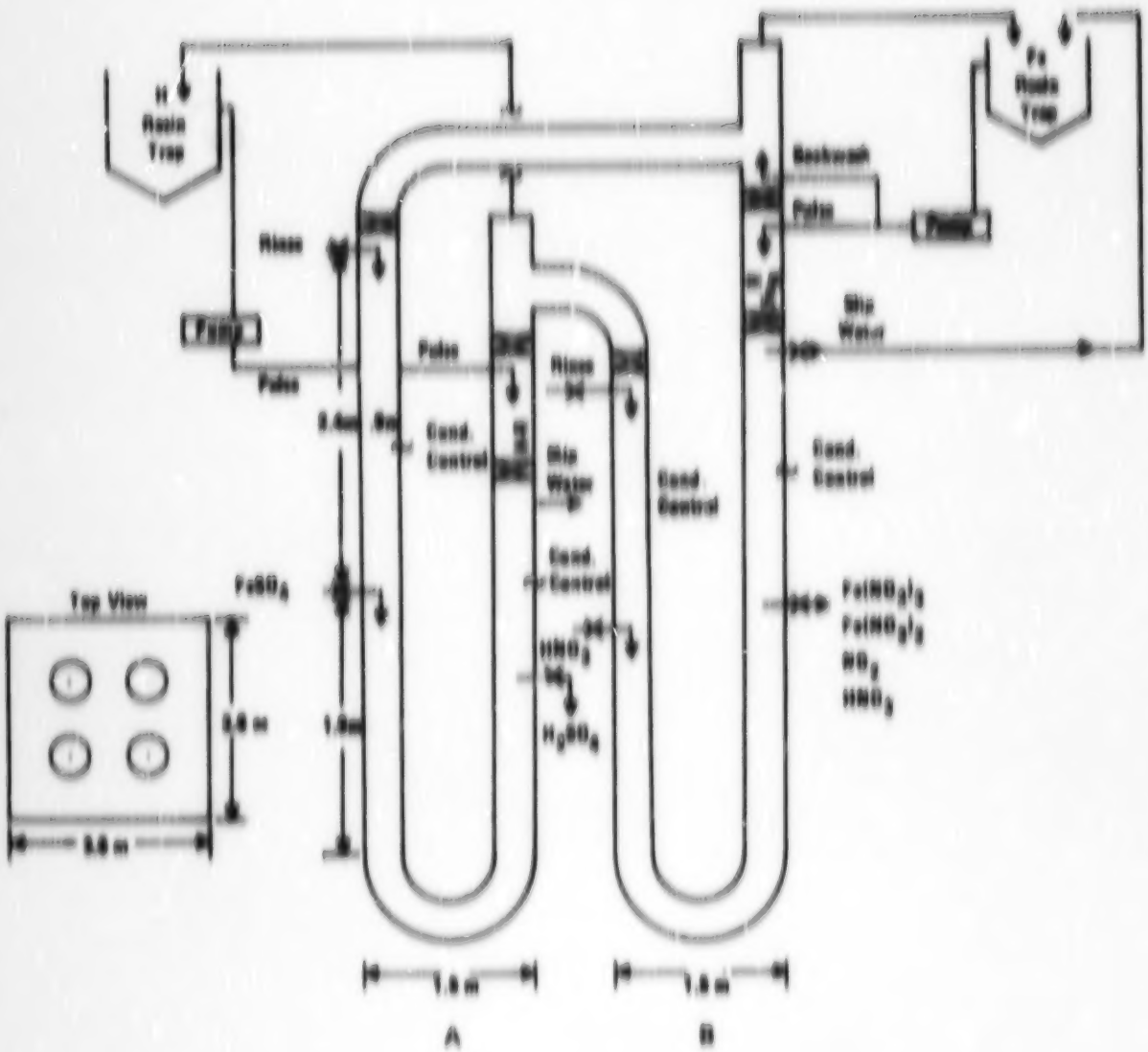


FIGURE 5. SCHEMATIC OF DOUBLE LOOP CONTACTOR
RESIN: DOWEX HGR-W, 500 mL R.

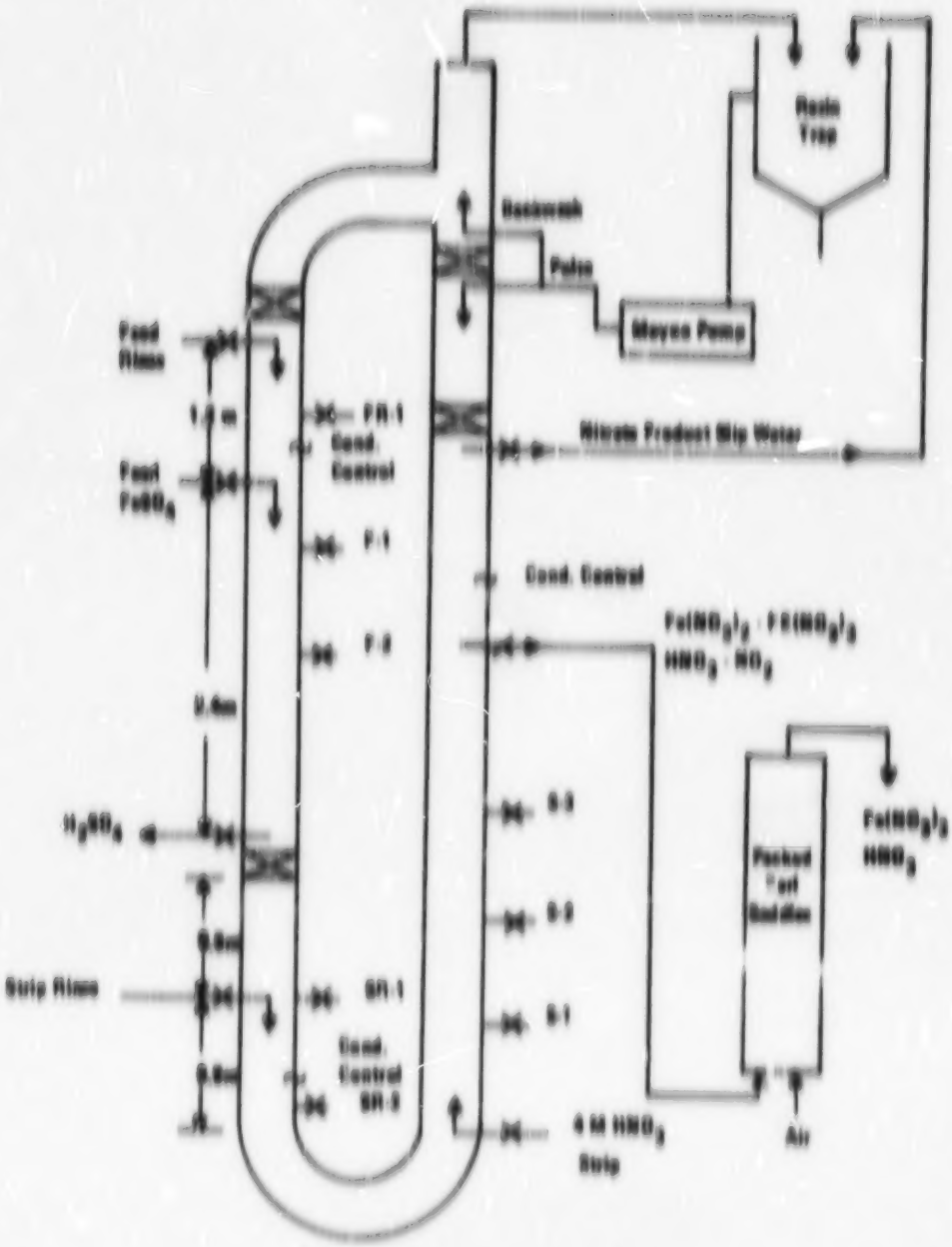


FIGURE 9A. SCHEMATIC OF PILOT PLANT CONTACTOR OPERATED FOR CONCENTRATED NITRATE PRODUCT DOW RESIN: HGR-W

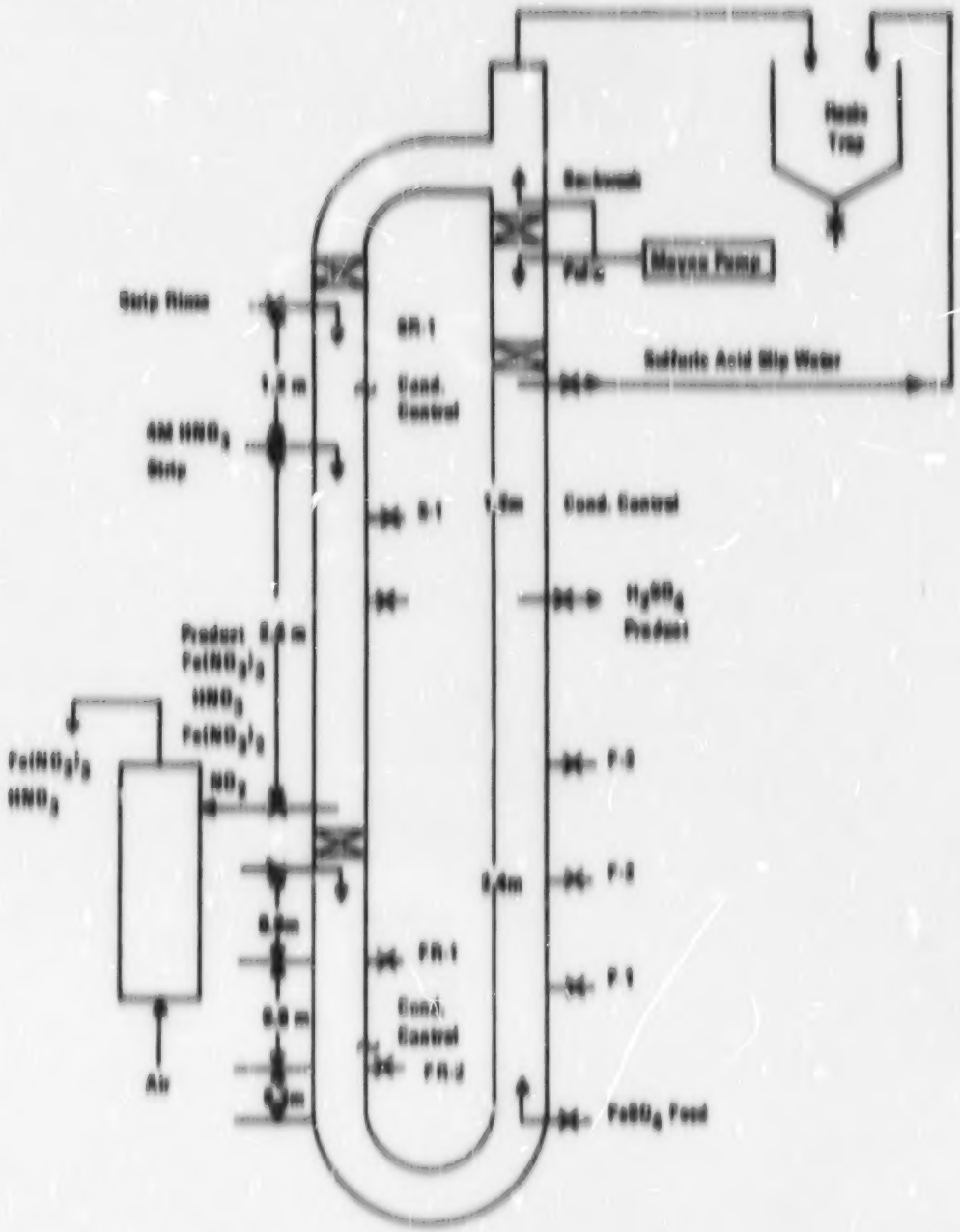


FIGURE 66. SCHEMATIC OF PILOT PLANT CONTACTOR
RESIN: DOW HRCW OPERATED FOR CONCENTRATED H_2SO_4

The unit will be 0.915 m (3 ft) in diameter and contain 14,150 liters (500 ft^3) of a cation exchange resin such as Dow HGR-X (a gel type resin). The unit will be fabricated from stainless steel.

5.2.3 Flow Rates in the Ion Exchange Unit

The feed is 16 liters/min (5 gallons/min) of approximately 2.5 Molar or 5 Normal ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) at 60°C. Only two runs were made at the proposed operating temperature of approximately 60°C after it was learned that 10 percent sulfuric acid was desirable. All others were run at 20°C. The design exchange capacity of the resin is 1.5 equivalents ("eq") of Fe^{++} per liter of resin. Consequently, the feed to resin flow ratio is

$$\left(\frac{1.5 \text{ eq/l resin}}{5 \text{ eq/l } Fe^{++}}\right)$$

or 0.3 and the resin flow rate is approximately 64.5 liters (17 gallons) per minute. A 75-percent excess of 4M nitric acid for stripping the iron from the resin is assumed, based on ferrous ion with a flow of about 41.8 liters (11 gallons) per minute

$$\left(\frac{4 \text{ eq/l} \times 41.8 \text{ l}}{1.5 \text{ eq/l} \times 64.5 \text{ l}} = 1.75\right).$$

It is assumed that the nitric acid regenerant will contain about 1 percent iron upon recycle from the hydrolysis unit.

5.2.4 Operation of the Unit

The ferrous sulfate solution is introduced into the left-hand part of the unit, as shown in Figure 5. It flows downward through a portion of the hydrogen ion loaded resin bed in the section of the unit labelled A in Figure 5.

Simultaneously, regenerated H_2SO_4 is withdrawn from the right-hand arm of A as shown in Figure 5.

Similarly, a portion of the resin loaded with ferrous ions is treated in part B of the unit with 4 Molar nitric acid, and the ferrous ions on the resin are replaced by hydrogen ions. The resulting product consisting of $Fe(NO_3)_3$, $Fe(NO_3)_2$, some NO_2, and HNO_3 is drawn off.

Rinse water for the ferrous ion loaded resin flows intermittently to A, the flow being controlled by a conductivity probe ("cond." in Figure 5) which serves to maintain the ferrous sulfate solution, water interface at a constant level. When on, the interface is displaced downward; when off, upward.

The H-resin above the sulfuric acid contains water in its void spaces (having been rinsed in B). When the rinse water is on, sulfuric acid flows if its exit valve is open. If it is closed, the slip cycle valve is open. Which valve is open is controlled by the conductivity probe at the sulfuric acid, water interface. When the slip cycle valve is open, the sulfuric acid displaces the H-resin water which flows out the slip cycle valve. This slip cycle water can be recycled. Its volume is equal to that of the rinse water, discounting a small dilution of the H_2SO_4 product. It contains only a small amount of acid or mineral ions. A similar rinse process occurs in B for the hydrogen ion loaded resin.

The flows of ferrous sulfate and nitric acid in A or B, respectively, are shut off and the resin beds are pulsed or shifted countercurrently. The valve above each rinse cycle is open while the resin is being pulsed. The rate of resin flow is determined by the feed/resin flow ratio discussed previously.

In A, a portion of the ferrous ion laden resin (Fe-R), with its void spaces containing water, flows overhead to the resin trap on the right (Fe-Resin Trap) to be fed to B. From B, a portion of the hydrogen laden resin flows to the resin trap on the left (H-Resin Trap), to be fed to A.

The overall process is repeated in short cycles.

5.4 OXIDATION UNIT

It is planned to heat the nitrate product from the ion exchange unit to 95°C before passing the product into a 10.16-cm (4-inch) diameter packed tower, 3.05 m (10 ft) high. Air will be blown through the tower at 10,613 liters (375 ft^3) per minute to oxidize ferrous ion and any nitrogen dioxide.

5.4 HYDROLYSIS (See Experimental Work)

A scraped coil continuous hydrolyzer will be used. The process design requirements will be determined from the experimental work reported. No analysis of the availability of suitable commercial equipment has been made yet.

5.5 SOLID-LIQUID SEPARATION

No work has been done to investigate the separation of the liquid HNO_3 and solid Fe_2O_3 coming from the hydrolyzer. It is felt that commercial equipment can be specified.

5.6 DRYING

No specifications for the drying step have been established.

5.7 PLANT COSTS

Very preliminary plant cost estimates have been made. They are shown in Tables 2 and 3. The estimates have been made by knowledgeable engineers. However, the availability and cost of commercial equipment or equipment design and construction cost would have to be firmed up considerably before a demonstration plant could be built.

The estimated total capital cost of the plant installed is $1,288,000.

The yearly operating costs (for 350 days) are estimated at $91,000.

The costs of the complete plant cover:

1) the acid recovery system,
2) the ion exchange system,
3) the hydrolyzer system.

[redacted]

[redacted]

[redacted]

TABLE 3. CAPITAL AND OPERATING COSTS (ION EXCHANGE ONLY)

CAPITAL COSTS

Chain-type CCCX Contactor	$350,000.00
Installation	$ 50,000.00
Start-Up	$ 50,000.00
	$450,000.00

OPERATING COSTS

	(Dollars/day)
Resin attrition - 3 years @$40/cu. ft. (28.3 liters)	20
Boric acid make-up @ 2%, @$0.60/lbs ($0.7 kg)	27
One operator/shift, plus supervision @$5/hr	120
Maintenance (Material & Labor)	
8% of equipment without exchange resin	45
Power — 50 hp @ 2¢/kWh	2
OPERATING COST PER DAY	$214

It is assumed that one operator per shift can operate the total plant. The plant would require 12 to 16 months to build and install. However, if the proposed demonstration plant could be located at the site of an existing low-temperature acid recovery plant, the estimated cost would be significantly reduced.

SECTION 6

EXPERIMENTAL WORK

6.1 ION EXCHANGE

6.1.1 Operation of Unit and Sampling

As noted, all of the experimental work was carried out in the single loop pilot plant equipment operated as shown in Figures 6A and 6B.

Studies aimed at the production of concentrated iron nitrate used the arrangement of Figure 6A, and those emphasizing the production of concentrated H_2SO_4 used the arrangement of Figure 6B.

The pilot plant unit is operated in essentially the same manner as that described in detail for the proposed double loop unit. However, there is an important difference. The rinse section lies between the two product solutions which are desired at a high concentration (or density).

Therefore, when operating as shown in Figure 6A, there is a much greater possibility for dilution of the sulfuric acid product than when operating as in Figure 6B for the dilution of the nitrate product. This is so since resin in which the void spaces are filled with water passes through the zone where the product above it is drawn off. This is the major reason for the proposed double loop unit.

The flow rates and analyses for the runs of this section are given in Tables 4, 5, and 6.

The unit was operated at steady-state flow conditions over a daily shift period.

Samples of the effluent products are taken each hour in order to get a material balance and an average analysis.

Near the end of the day, samples (called profile samples) are taken around the loop.

Profile samples are taken consecutively at 0.61-m (2-foot) intervals downstream from the point of solution entry, as indicated in Figures 6A and 6B.

TABLE 4. DAILY AVERAGE FLOW RATES - ml/min

Code	Feed (Fe^{+3})	Product (H_2SO_4)	Strip (HNO_3)	Product (Fe^{+3})/(Fe^{+3})$_0$	Product Strip Water	Resin	Remarks
5-8	326	1350	279	408	241	400	Figure 2A
9-12	338	1740	330	341	275	400	
13-17	254	930	360	246	374	400	
18-21	166	867	340	46	316	400	
22-27	220	720	705	342	252	400	
28-34	231	288	310	325	256	400	Figure 2B
35-38	166	288	325	317	269	400	
39-41	165	125	298	360	250	400	Figure 2A
42-46	165	416	371	367	241	400	
48-51	239	402	324	325	304	400	
52-55	186	450	310	350	225	400	50% Fresh Acid
							25% Recycle Product Acid
56-58	176	360	454	441	250	400	60% Fresh Acid
							40% Recycle Product Acid
59-62	132	140	362	408	250	400	Heated Feed
63-65	118	70	367	417	233	400	No Rinse -- Heated Feed

TABLE 5. DAILY AVERAGE ANALYSIS OF INLET STREAMS

	Feed		Strip	
Code	N $FeSO_4$	Fe^{II} g/l	H^+ N	Fe^{III} g/l
5-8	2.82	76	4.10	--
9-12	2.82	76	4.10	--
13-17	2.80	--	3.84	--
18-21	2.80	--	3.91	--
22-27	2.99	76	3.93	--
28-29	2.99	76	3.99	--
30-34	2.99	76	4.00	--
35-38	2.99	76	4.00	--
39-41	2.82	80	4.00	--
42-46	2.73	--	4.0	--
48-51	2.70	--	3.7	--
52-55	2.90	85.5	3.67	7.0
56-58	2.90	85.5	3.70	14.2
59-62	4.62	133	4.0	--
63-65	4.62	133	3.77	--

TABLE 6. DAILY AVERAGE ANALYSIS - EXIT STREAMS

	Nitrate Product			H_2SO_4 Product			Slip Water		
	TM+H	Fe	NO_3	TM+H	Fe	NO_3	H^+	Fe	NO_3
Code	eq/l	g/l	g/l	eq/l	g/l	g/l	eq/l	g/l	g/l
5-8	2.34	31.7	125	0.83	2.7	9.0	--	4	0.10
9-12	3.42	70.5	198	1.03	10.2	5.8	--	0.64	0.03
13-17	3.31	64.0	190	0.97	15.8	0.95	--	2.4	2.0
18-21	3.60	79.0	180	0.63	8.5	6.5	--	2.4	2.5
22-27	3.60	29.0	230	1.00	2.7	1.6		1.1	2.0
30-34	3.14	27.0	150	2.54	12.6	6.6	--	0.4	1.9
35-38	3.59	58.0	210	2.67	7.5	17.0	0.45	0.78	3.1
39-41	3.10	31.0	140	0.51	0.8	1.3	0.08	29	5.0
42-46	3.54	25.0	175	1.24	3.6	2.7	0.05	0.68	2.7
48-51	3.18	57.3	183	1.80	7.0	26.0	0.04	--	0.8
52-55	3.47	44.3	165	1.34	6.5	6.2	0.05	0.05	0.15
56-58	3.44	39.0	158	1.33	11.1	2.8	0.06	0.08	0.33
59-62	3.77	41.6	215	2.12	10.6	9.8	0.09	0.75	1.3
63-65	3.59	39.5	340	3.29	12.5	4.3	0.07	0.04	0.3

6.1.2 Loading Conditions and Preparation of Sulfuric Acid

In most of the runs reported herein, a tank of saturated $FeSO_4$ solution at 20°C was used as feed. Under these conditions, the feed was about 2.8N. Therefore, the H_2SO_4 product could not be greater than 13 percent (see Figure 7).

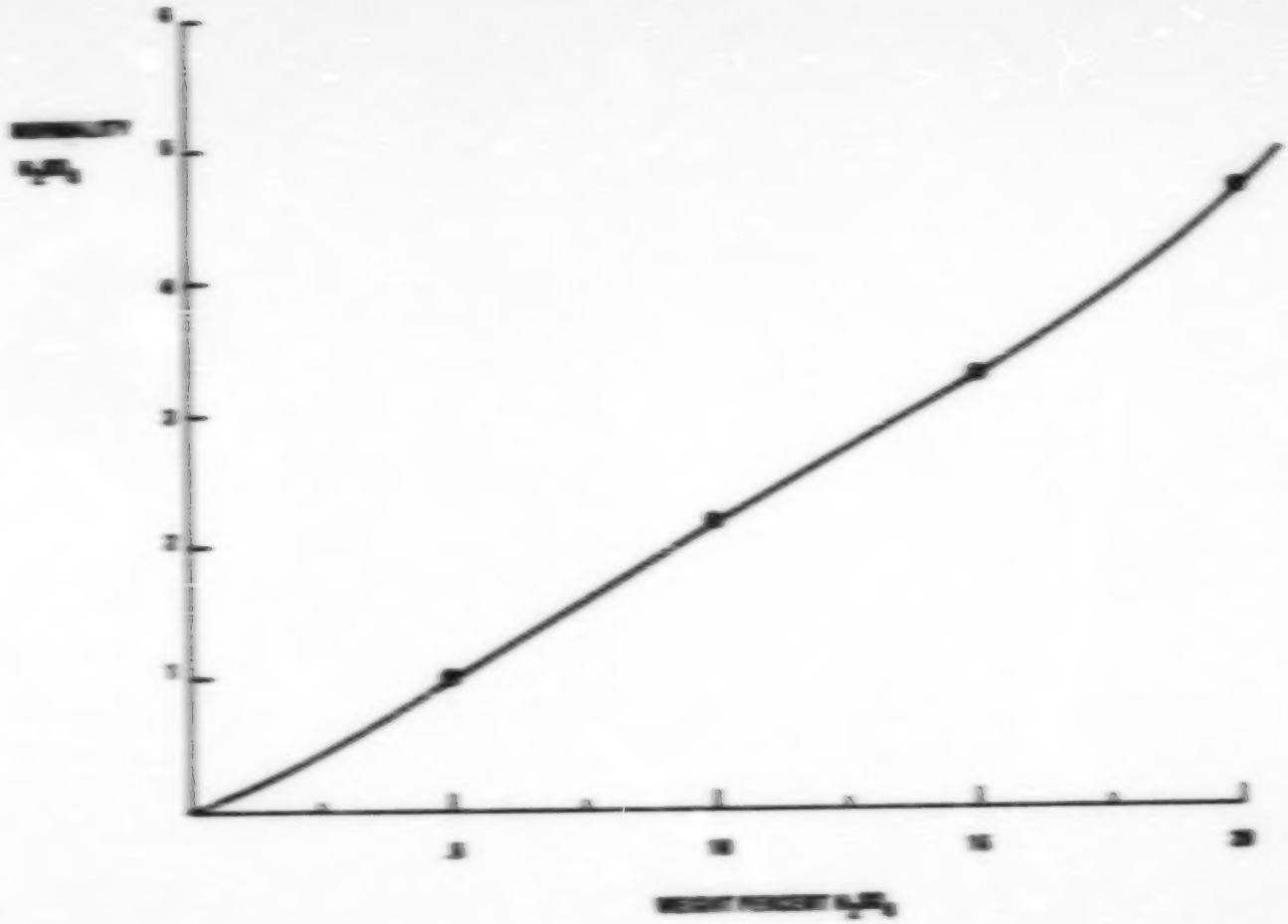
The results under these conditions of the two successful runs to maximize H_2SO_4 concentrations are shown in Figures 8 and 9, and in Tables 4, 5, and 6, Code Numbers 30-34 and 35-38.

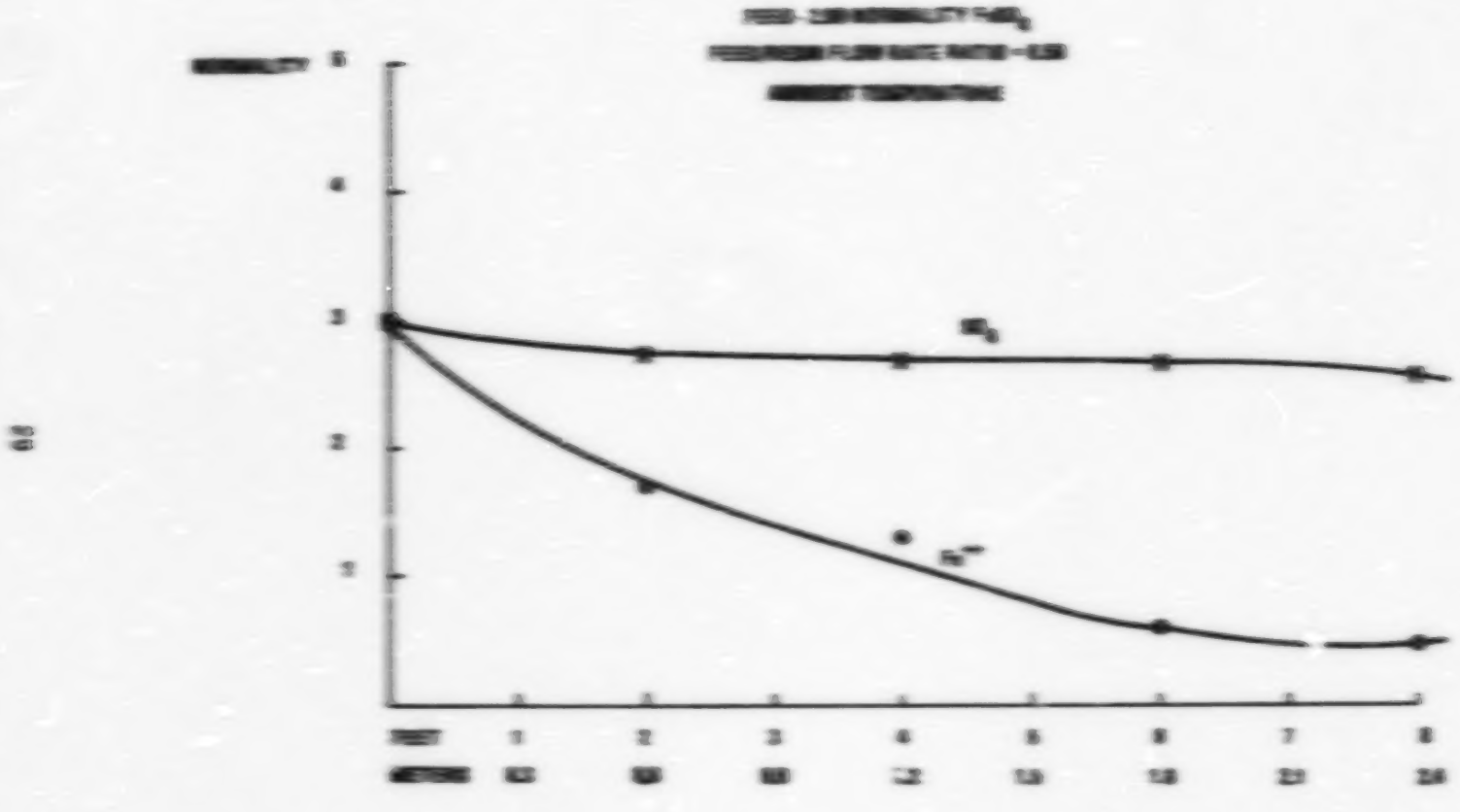
For example, see Figure 9. Samples of the product are taken at F-1, F-2, and F-3 and at the H_2SO_4 exit valve (0.61-m (2-foot) intervals) in Figure 9B. These samples are analyzed for $SO_4^=$ by the Total Mineral (T.M.) method and for iron by the ortho-phenanthroline method (see the Analytical Methods Section).

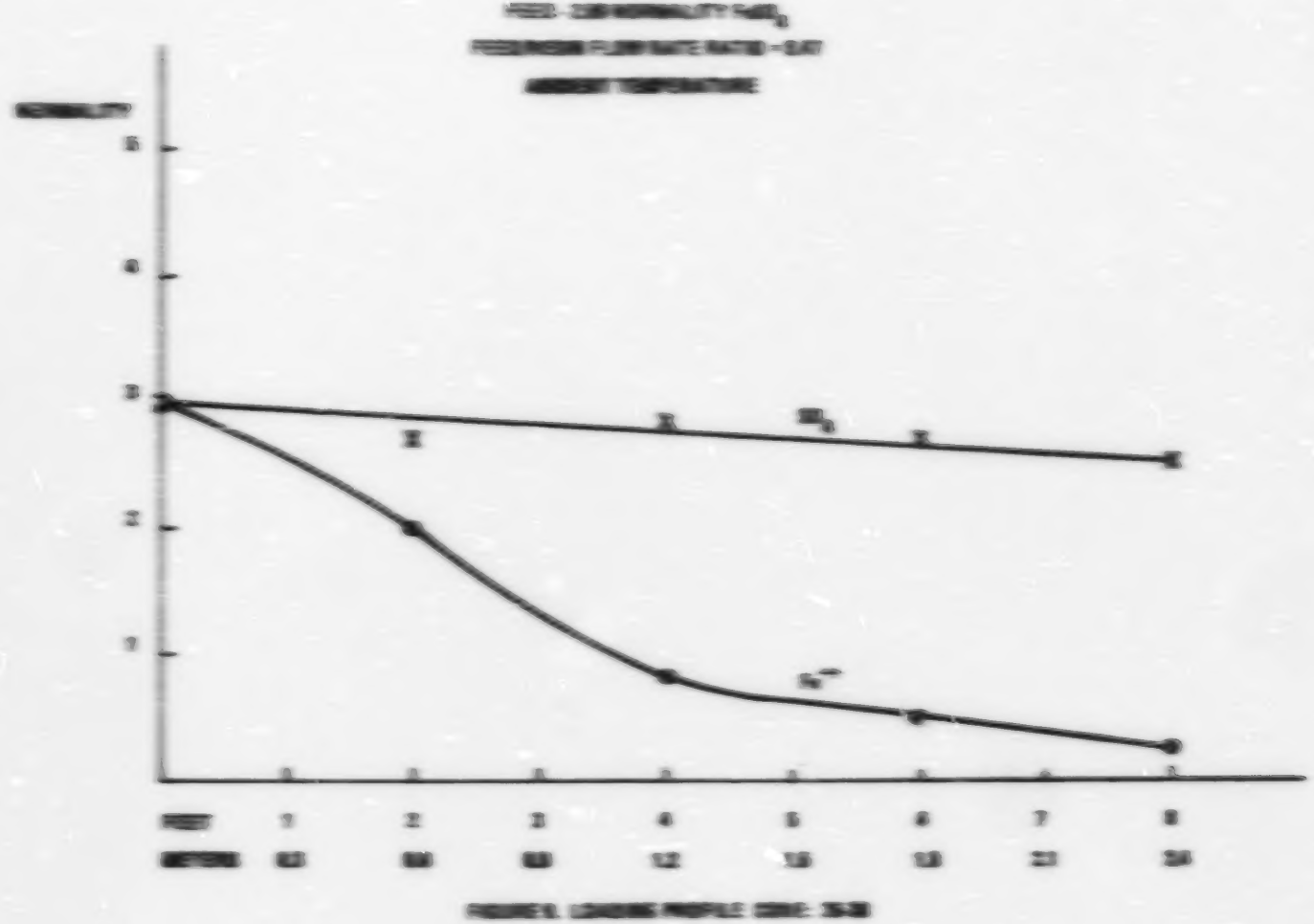
The product, from the curve, is about 2.5N in $SO_4^=$ concentration, equivalent to about 11.5 percent by weight H_2SO_4. The dilution of the 3N $SO_4^=$ feed to 2.5N $SO_4^=$ product by the slip water is obvious. The iron content of the product is low, it generally being of the order of 10 percent by weight of the H_2SO_4.

It is postulated by the authors that some oxidation of the ferrous ion by HNO_3 occurs during the stripping or resin regeneration step. Subsequent hydrolysis leads to the formation of a species of Fe_2O_3 which is insoluble in HNO_3 and which is occluded in the resin matrix. This Fe_2O_3 is carried around the loop in the matrix of the resin and is dissolved by the strong H_2SO_4 product, thus accounting for the iron in the H_2SO_4 product.

It was learned by Crown during these studies that an 18 percent by weight H_2SO_4 product was desirable. In order to avoid the use of an evaporation step, two attempts were made to make a stronger product by heating the $FeSO_4$ feed tank with a stainless steel coil to 60°-65°C with agitation. Between 60° and 80°C, $FeSO_4$ has a limiting solubility of about 6.6N. The conditions used were a temperature of 62°C and a concentration of $FeSO_4$ of 4.62N. These conditions are close to the proposed plant conditions. The runs were made so as to maximize nitrate product.







The results obtained are shown in Figures 10 and 11 and Tables 4, 5, and 6, Code Numbers 59-62 and 63-65 with Run 63-65 producing about 15 percent H_2SO_4. The iron concentration drops very rapidly along the resin bed, as can be seen in Figures 10 and 11, showing a high rate of exchange with the resin. This is probably due to the higher temperature.

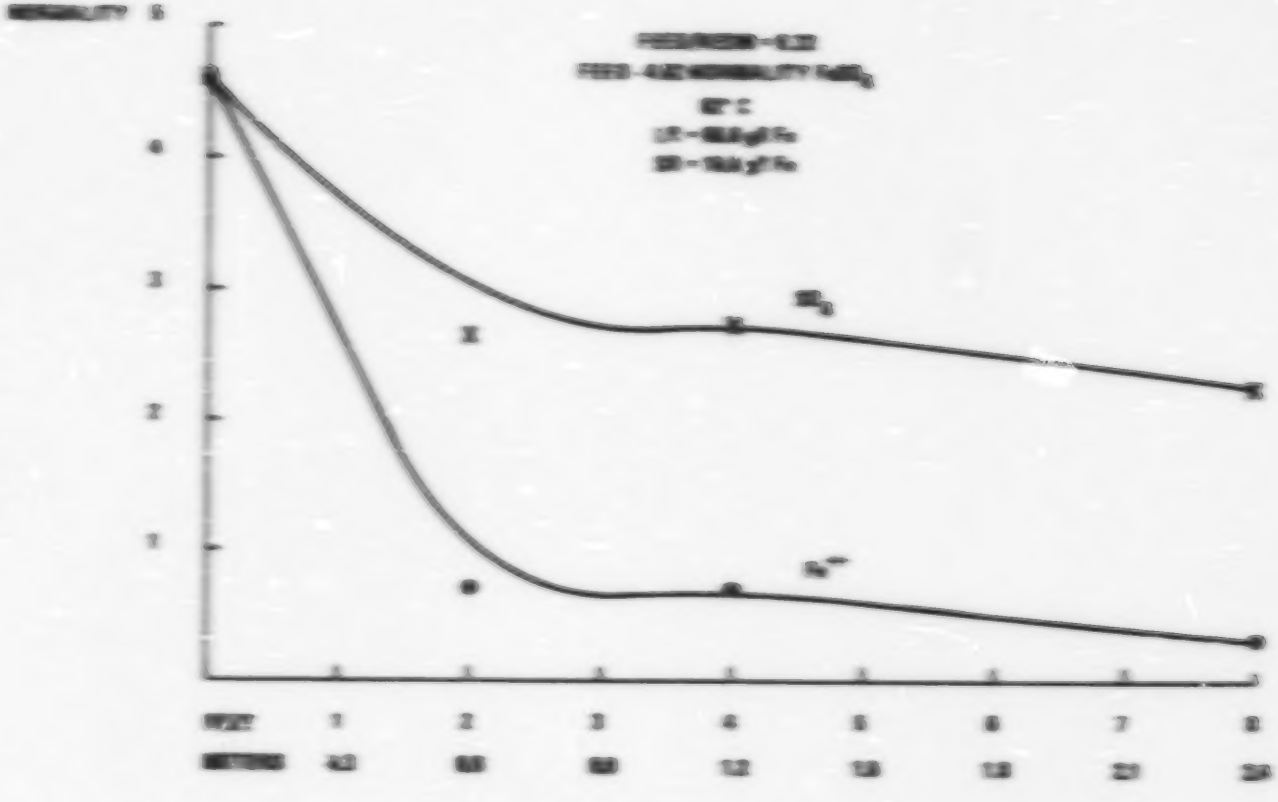
6.1.3 Stripping Conditions

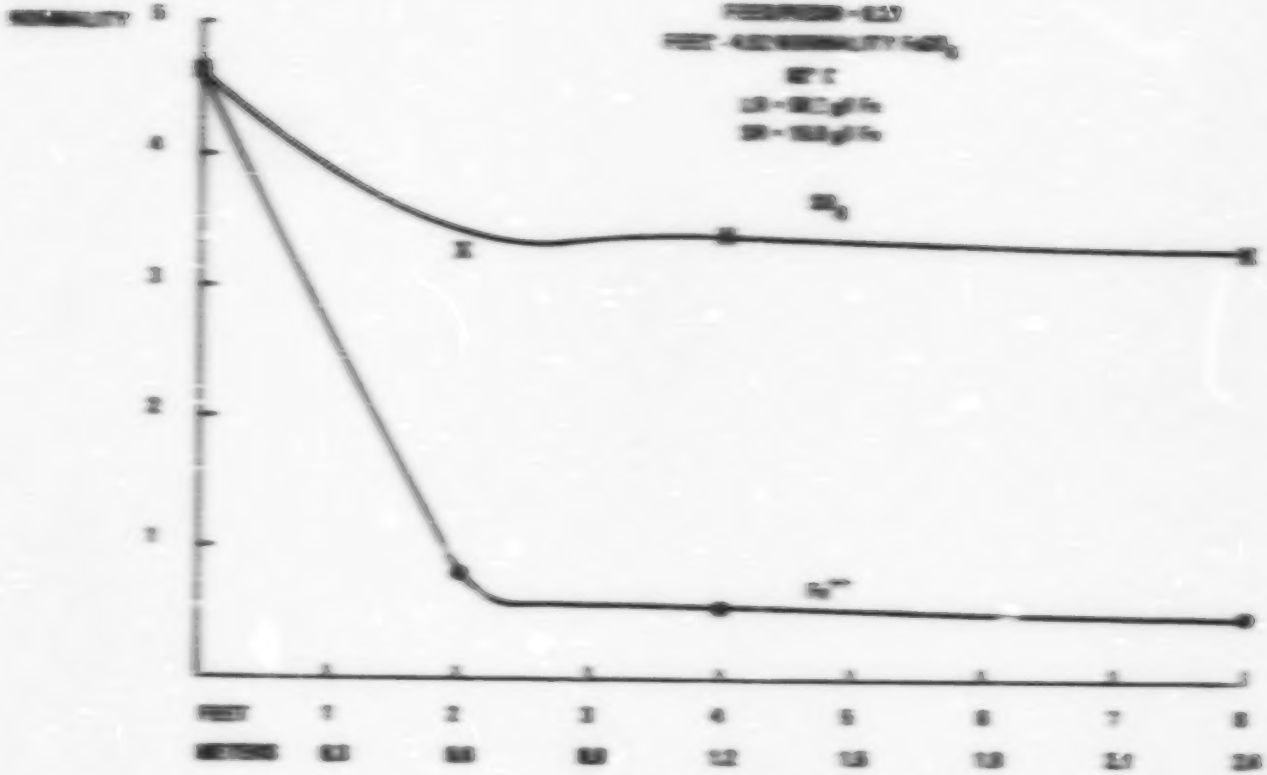
It is desirable to use the minimum excess HNO_3 required to leave a minimum of unstripped iron on the resin. There is a limit to the extent of iron removal regardless of the amount of HNO_3 used.

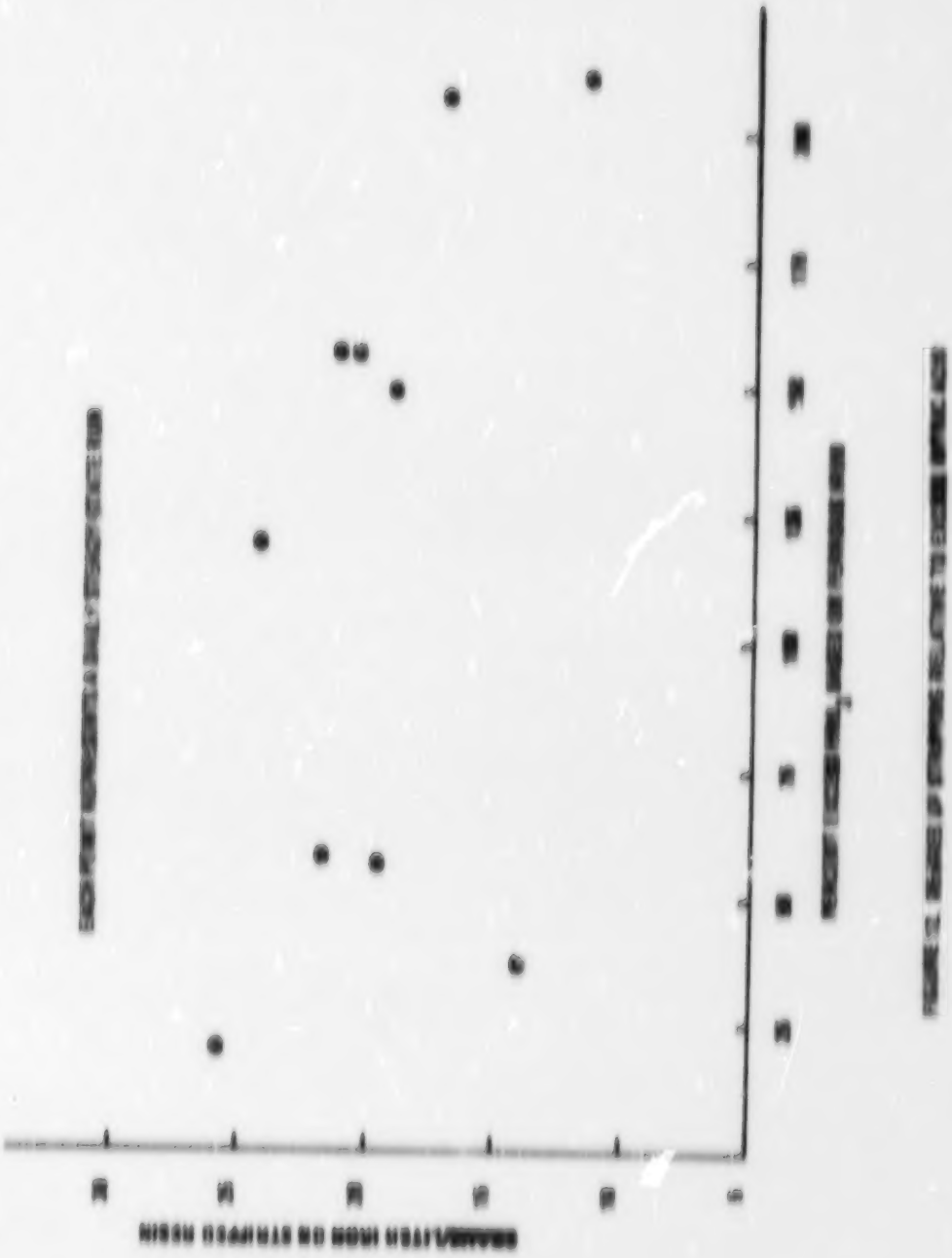
This is shown by the data for 10 runs in which the amount of iron remaining on the resin after stripping was determined. The procedure used was to complete the removal of the iron by stripping the regenerated resin with H_2SO_4 or HCl and determining the removed iron by the ortho-phenanthroline method. In all of the runs, the concentration of the HNO_3 was approximately the same (4M) as was the $FeSO_4$/resin flow ratio. The data are summarized in Figure 12 and Table 7. Analysis of the experimental points shows little or no difference between the amount of iron retained on the resin between an excess of HNO_3 of 50 percent and 150 percent.

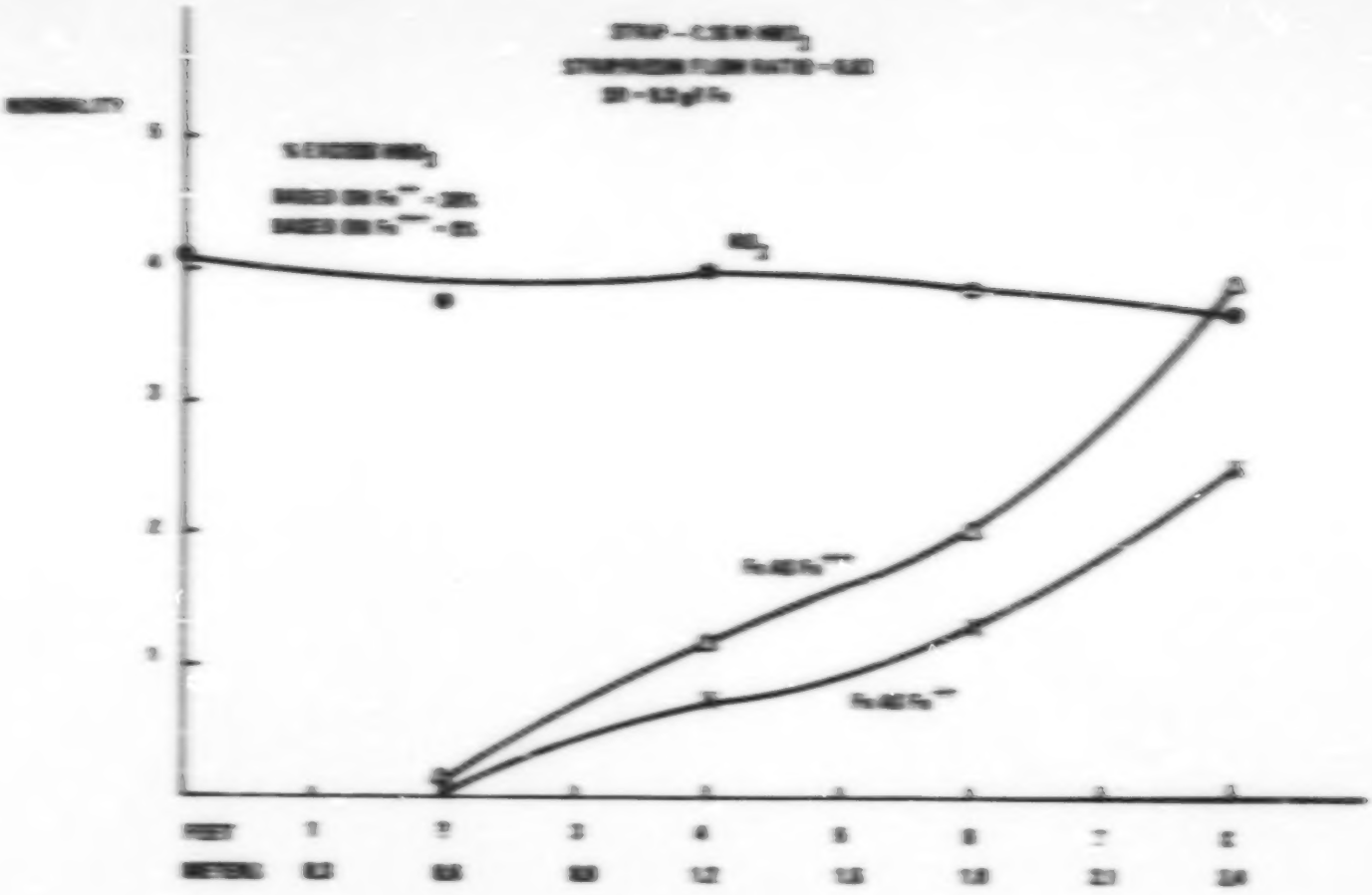
The strip profiles of Figures 13, 14, and 15 show typical events of the stripping process. Note that the normality of the replaced iron solution cannot be greater than the normality of the stripping acid. Referring to Figure 13, for example, it is seen that the stripping acid/resin flow rate is 0.83. Therefore 3.4 equivalents of HNO_3 have replaced approximately 2.5 equivalents of Fe^{++} at the 2.4-m (8-foot) product exit of the column. Therefore, we have an excess of 36 percent HNO_3 (3.4/2.5 = 1.36 or 136 percent) based on ferrous ion. The percent excess HNO_3 cannot be determined exactly since both ferrous and ferric iron are probably present. Some attempt was made to determine the fraction of Fe^{++} and Fe^{+++} ions emerging from the ion exchange unit, but the results varied from 50 to 90 percent oxidation. Therefore, it is necessary to use an oxidation tower for this reason as well as to oxidize NO_2.

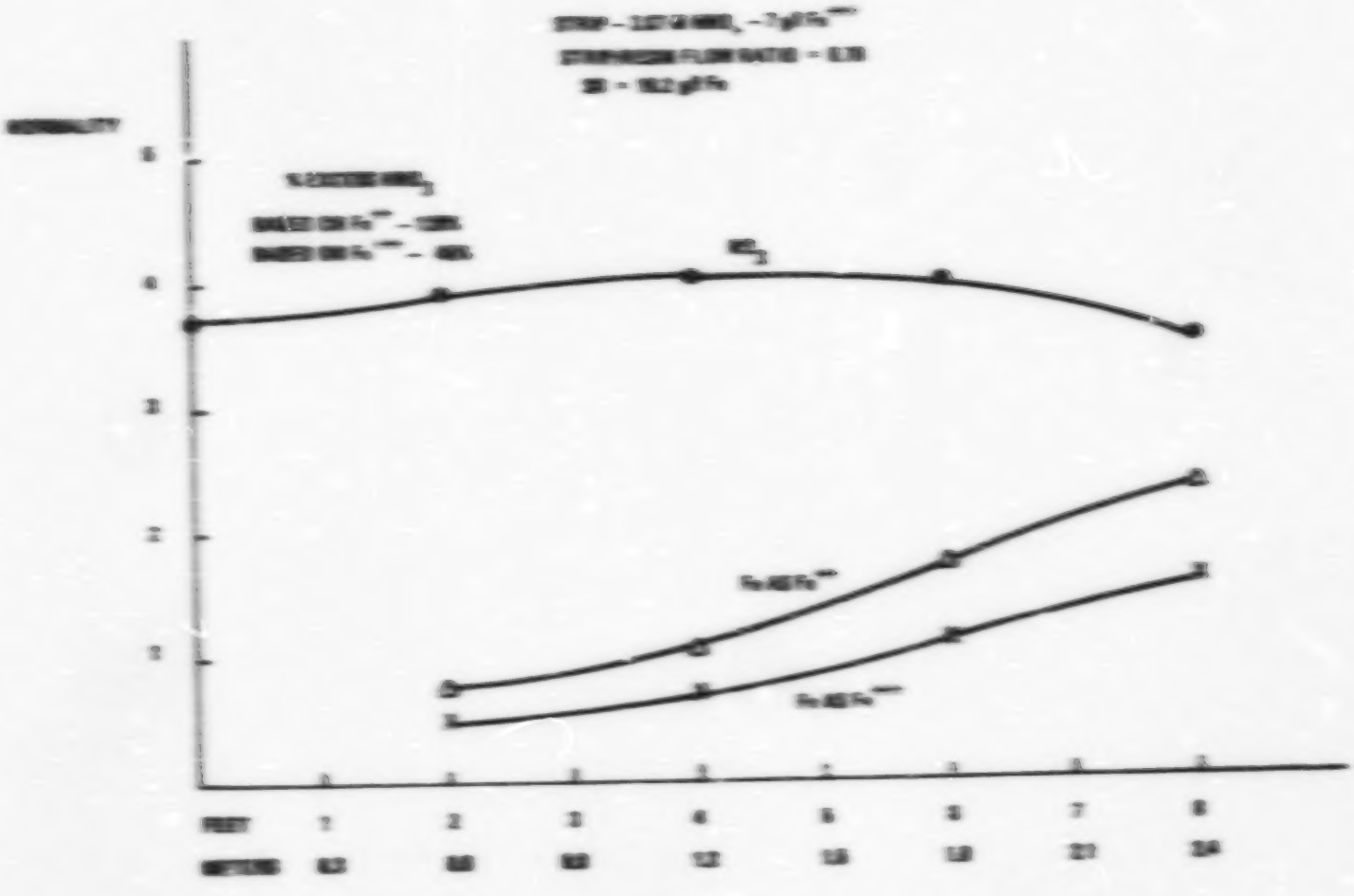
There is a slight dilution of the total nitrate near the product exit. This is due to dilution by the slip water. However, the nitrate strength is easily made up during the blowdown from the hydrolyzer.











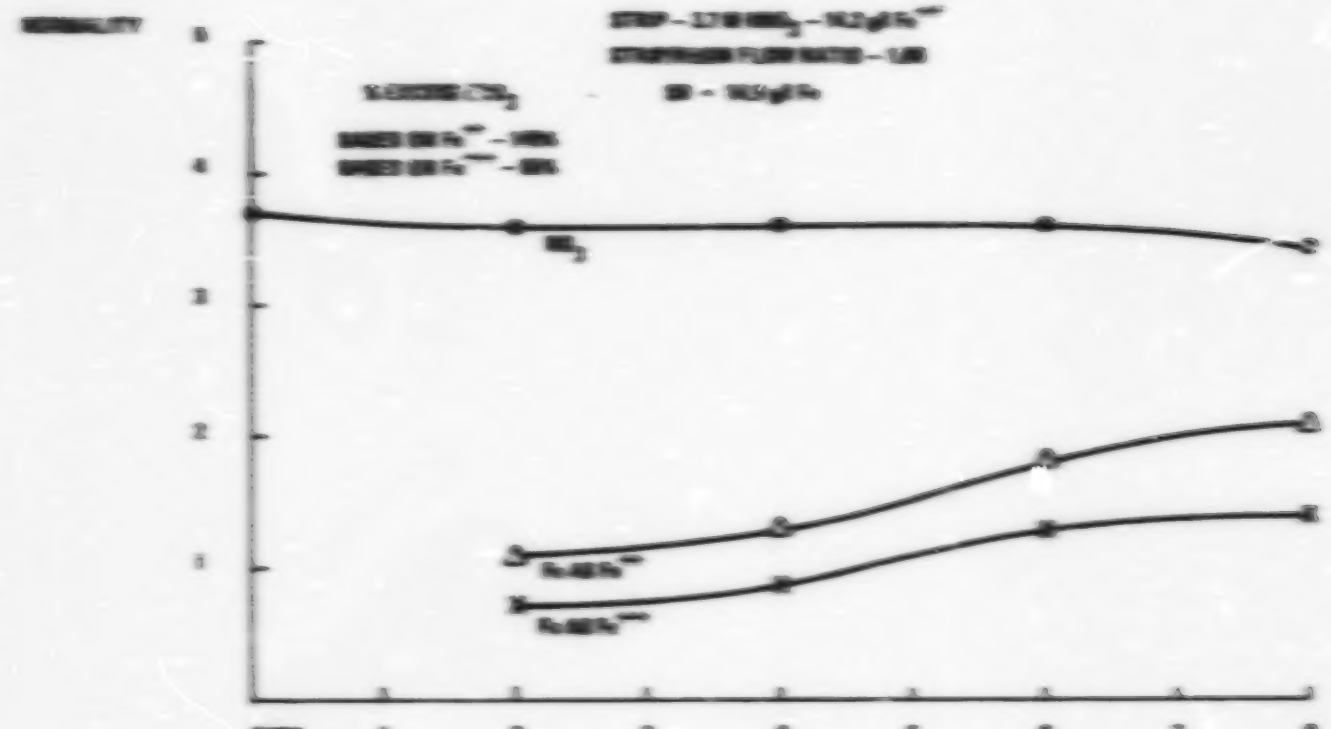


TABLE 7. IRON ON STRIPPED RESIN

Code	% Excess Nitric Acid	HNO_3 Concentration	g/l Iron on Stripped Resin	HNO_3/resin Flow Ratio
9-12	36	4.10	9.0	0.83
13-17	59	3.84	10.8	0.75
18-21	24	3.91	20.8	0.85
22-27	220	3.93	6.5	0.76
30-34	212	4.00	12.6	0.93
48-51	66	3.70	14.4	0.81
52-55	120	3.87	19.2	0.78
56-58	149	3.70	14.0	1.06
59-62	156	4.00	16.0	0.96
63-65	166	3.77	16.0	1.04

In the runs where the strip nitric acid was a simulated hydrolysis product (Figures 14 and 15), the effect is a tailing of iron at the 0.61-m (2-foot) mark.

The accuracy of the analyses and measurements of Sections 2 and 3 as well as the efficiency of the process is shown by the data of Tables 4, 5, and 6.

For example, consider the run of Code 59-62. This is a warmed (62°C) run to maximize iron nitrate production.

The feed is 0.132 l/min of 4.62N $FeSO_4$ or 0.61 eq/min, equal to 17.1 g/min of iron.

The product is obtained at 0.408 l/min at a concentration of 41.5 g/l of iron. Therefore, 17.0 g/min are produced.

The slip water flows at a rate of 250 ml/min and contains 0.75 g/l. Therefore, 0.19 g/min pass in the slip water. The material balances are excellent.

6.1.4 Resin Capacity and Stability

A cost factor of major concern is related to the stability of the resin. In a previous study [2], fixed beds of new resin and resin used for approximately 6 months were loaded rapidly with dilute $FeSO_4$ solution. The ion exchange capacity measured from both loading and stripping was about the same (1.75 eq/l). The rate of exchange was actually a little faster on the used resin.

A sample of the used resin was sent to the Dow Chemical Company for evaluation. It was not out of specifications in any way compared to new resin, as shown in the following analysis:

H-form capacity = 2.06 eq/l
Na-form capacity = 2.20 eq/l
H-form 47% water (47% to 50% is standard)
98% whole beads (1% broken beads)

If extended studies show significant breakdown, alternative resins are available. However, at the moment, the life of the resin does not seem to be an important factor.

6.2 OXIDATION TOWER

In the oxidation of ferrous ion by nitric acid, nitrogen dioxide is formed. A small, packed column was used at the ion exchange product outlet, and the nitrate product was heated and blown with air to oxidize the NO_2 to HNO_3 and the ferrous to ferric ion.

A nitrate ion selective electrode was used to follow nitrate material balance (see Analytical Methods). Nitrate material balances before and after use of the packed tower are shown in Table 8. Nitrate recovery is nearly 100 percent when using the tower.

6.3 HYDROLYSIS

The basis for this work is a patent owned by the Bethlehem Steel Corporation [4].

Ferric nitrate produced by the ion exchange unit is decomposed thermally. The nitric acid produced is returned to the ion exchange unit for resin regeneration. The ferric oxide produced may be an attractive commercial product.

The nitric acid, ferric nitrate liquors used were from Chemical Separations Corporation work. The initial experiments were conducted in a 300 ml autoclave (see Figure 16).

A thermocouple was installed within a sheath probing the autoclave cavity. It was connected to a -17.8°C to 242°C Honeywell Indicator.

A second thermocouple was attached to the furnace and connected to a -17.8° to 1025°C Fenwall Controller in order to insure that the furnace was not heated excessively. The controller was set at 512.5°C. The heat-up time for the contents of the lead-jacketed vessel was over 20 minutes.

It was determined that the precipitate formed in the hydrolyzer was ferric oxide and not ferric hydroxide.

However, with this apparatus it could not be determined if the conversion occurred within the liquid at 205°C or at the vessel wall at 512.5°C.

Nitrogen dioxide was observed emerging from the discharge of the pressure vessel. Therefore, the process may require a scrubber or oxidizer of some sort behind the hydrolyser.

TABLE 8. NITRATE MATERIAL BALANCE BEFORE AND AFTER USE OF OXIDATION RECOVERY TOWER

Code	Percent Recovered NO_3	Remarks
5-8	70%	Before use of Tower
9-12	88	
13-17	85	
18-21	83	
22-27	100	After Installation of Tower
28-29	118	
30-34	82	
35-38	87	
39-41	102	
42-46	88	
48-51	86	
52-55	107	
56-58	97	
[illegible]-62	101	
63-65	102	

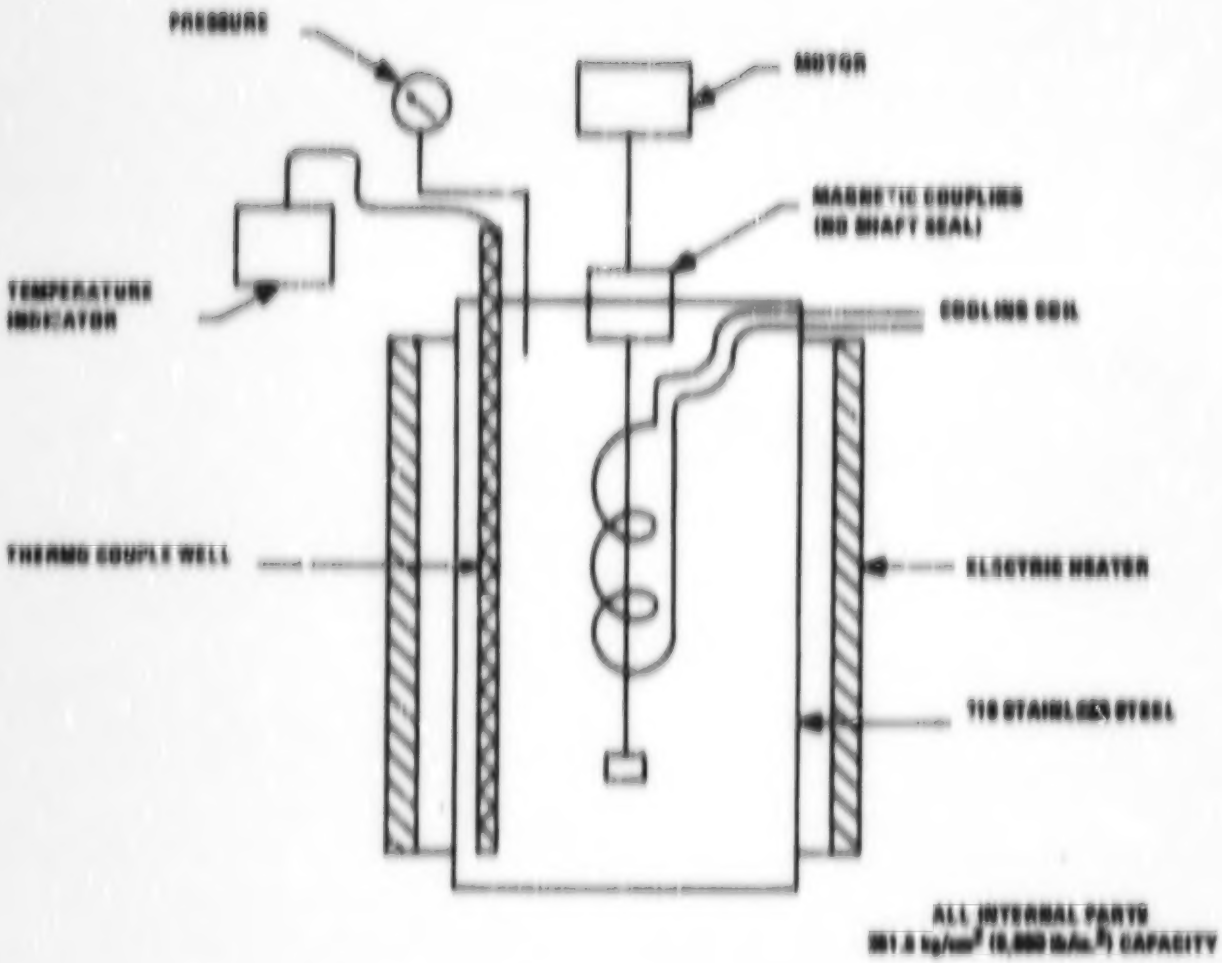


FIGURE 18. LABORATORY HYDROLYSER 300 ml CAPACITY

To determine the lowest efficient hydrolysis temperature, a 3.8 liter (1 gallon) continuous coil (1.6 cm (5/8 in.) - 316 stainless) autoclave was constructed. A schematic of the apparatus is shown in Figure 17. This coil was small enough in diameter to provide essentially instantaneous heat up to the 205°C of the Dowtherm constant temperature bath. The pressure differential of input and output determined the flow rate. At a rate below 7.6 liters (2 gallons) per hour, the tube clogged. At a rate much greater than 7.6 liters (2 gallons) per hour the conversion to Fe_2O_3 was incomplete.

Three hundred runs were conducted to convert ferric nitrate to ferric oxide, 254 in the batch unit and 46 in the continuous unit.

An average of 20 percent by weight HNO_3 was recovered in these runs.

The produced iron oxide contained adsorbed nitrates. After drying at 200°C for 1 hour, about 99 percent Fe_2O_3 could be produced. There is no difference if the Fe_2O_3 product is dried at 550°C. However, it is clear that a drying step will be necessary in the process. An average analysis of the best 20 successful continuous runs is given in Table 9. The Fe_2O_3 has an average purity of 98.8 percent which is suitable for pigment. Analysis of the Fe_2O_3 was performed by Crown; Pfizer, Inc.; and G. A. Laboratories.

TABLE 9. FINAL CONTINUOUS HYDROLYZER TEST REPORT

SUMMARY OF 20 MOST SUCCESSFUL RUNS

AVERAGE INPUT 2000 ml $Fe(NO_3)_3$ Coil Wall Temp. (205°C)

CONTACT TIME: PRESSURE:

10 min 10.6 kg/cm^2 (150 lb/in^2)

ANALYSIS OF COMPOSITE SAMPLE	Fe_2O_3	AVERAGE NITRIC ACID ANALYSIS
$\%Fe_2O_3$	98.8	20.6 $\%HNO_3$
Color	Red	1.5 %Fe
Total Sample	20 g	Yellow Color

SECTION 7

ANALYTICAL METHODS

Acid concentrations were determined by standard acid-base titrations.

All iron was determined by the standard ortho-phenanthroline colorimetric method [5]. In this method the ortho-phenanthroline is sensitive only to the ferrous ion. However, both ferrous and ferric ions may be determined by leaving out or adding the hydroxylamine-hydrochloride reducing agent. In this study a considerable number of inconsistencies were observed, and it was not possible to determine accurately the ferrous/ferric ion ratio at the contactor exit. But for total iron, the method is highly accurate.

Nitrate ion was determined by using a Corning ion selective electrode with a Model 404 Orion meter. The method is sensitive and accurate. It is important to check frequently with a standard. Interferences are well eliminated by setting the instrument to read low ppm levels (0-100) and making large dilutions.

Where acid (H_2SO_4 or HNO_3) and Fe^{++} or Fe^{+++} are present together, a total mineral (acid and metal ions) analysis was made (T.M.). The solution is passed through a column of cation exchange resin. The metal ions are exchanged for hydrogen ion. The resulting acid is titrated with base. The method is simple and accurate. All free acid must be rinsed from the column, and the resin cannot be overloaded with the iron ions.

Analyses of the Fe_2O_3 product were made by outside analytical laboratories.

SECTION 8

PRELIMINARY MARKET ANALYSIS

8.1 INTRODUCTION

Crude iron oxide (Fe_2O_3 or ferric oxide) exists in the natural state as a mineral deposit. It is also produced synthetically by various chemical processes. Purity, color, and many other characteristics differ widely from source to source in both natural and manufactured materials.

Processing companies convert these crude materials into finished iron oxide by various operations such as washing to remove impurities, grinding to a smaller particle size, blending for shading and color tone or desired magnetic properties, weighing, packaging (usually 50-pound (22.7 kg) paper bags), and identifying by marking of containers.

The processors sell the finished iron oxide to manufacturers who use it as a color pigment in their products. They also sell finished iron oxide to manufacturers of ferrites, who use the Fe_2O_3 as raw materials having ferromagnetic properties.

Most finished iron oxide, whether for use as color pigment or ferrite starting material, is the product of skillful blending by the processors, who work very closely with their customers to satisfy individual requirements. This implies a high technical service ability.

Based on a survey by the National Paint, Varnish, and Lacquer Association and on a status report by Philips Laboratories on magnetic ceramics (including those produced from ferrites), the end-use markets for natural and synthetic iron oxides are estimated to be in the following proportions.

40% ferrite starting materials;
40% color pigments for nonpaint products (ceramics, rubber, mortar, etc.);
20% color pigments for paint, lacquer, and primers.

8.2 IRON OXIDE PIGMENT SALES

Table 10 from a recent Bureau of Mines publication [6] shows the finished iron oxide pigments sold by the processors in the United States in 1975. The quantity of natural and synthetic pigments was about the same 40,815-45,350 t (45,000-50,000 short tons). However, the value of the natural pigments was approximately $150 per ton or $0.165 per kg while that of the synthetic pigments was approximately $750 per ton or $0.822 per kg.

These data are in line with the sales price information received by Crown from various processors as shown below:

% Iron Oxide Purity	$/ton	$/kg
94	150	0.165
96	200	0.220
98	250	0.276
99	600	0.660
99[1]	800	0.882

Table 11 from the same Bureau of Mines publication [6] gives salient iron oxide pigment statistics. The value of all finished pigments sold was approximately $450 per ton or $0.496 per kg.

However, for 1975 the first information on iron oxides from steel plant wastes (dusts and regenerated pickle liquor) is shown in Table 11. Production by four steel companies was approximately 17.233 million kg (19,000 tons) with a value of approximately $1 M. This gives a value of approximately $0.055 per kg ($50 per ton). The product was sold principally for use in ferrite manufacture.

The value of the product that might be produced by the proposed process is undetermined. This uncertainty is probably an order of magnitude. Probably, a much larger sample should be produced and submitted to a number of processors before a more accurate value can be placed on the product. An accurate market evaluation may require a pilot plant or demonstration plant to be built.

TABLE 11. FINISHED IRON OXIDE PIGMENTS SOLD BY PRODUCERS IN THE UNITED STATES, BY KIND

Pigment	1974[r]		1975	
	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)
Natural:				
Brown:				
Iron oxide (metallic)[1]	13,016	2,342	10,545	2,007
Umbers:				
Burnt	5,754	1,033	3,964	1,026
Raw	1,937	662	1,454	542
Red:				
Iron oxide[2]	34,957	2,829	28,486	2,364
Sienna, burnt	964	475	682	338
Yellow:				
Ocher[3]	7,294	678	4,224	477
Sienna, raw	1,855	379	638	305
Total Natural	64,777	8,833	46,928	7,434
Synthetic:				
Brown: Iron oxide[4]	9,121	6,703	5,738	4,494
Red: Iron oxide	33,651	19,885	28,536	18,927
Yellow: Iron oxide	37,525	19,349	19,303	18,998
Total Synthetic	79,388	44,945	45,629	32,419
Unspecified, including mixtures of natural and synthetic iron oxides	8,467	5,839	9,383	6,755
GRAND TOTAL	147,544	61,672	104,840	46,206

[r]Revised.

Source: U. S. Bureau of Mines [6].

[1]Includes black magnetite and Nanjole brown.

[2]Includes sprite cinder.

[3]Includes yellow iron oxide.

[4]Includes black magnetite.

TABLE 11. SALIENT IRON OXIDE PIGMENTS STATISTICS IN THE UNITED STATES

		1971	1972	1973	1974	1975
Mine production	short tons	W	W	W	W	38,075
Crude pigments sold or used	do.	W	W	W	W	34,805
Value	thousands	$ 425	$ 418	$ 937	$ 1,429	$ 1,065
Iron oxides from steel plant wastes	short tons	W	W	W	W	19,252
Value	thousands	W	W	W	W	$ 1,102
Finished pigments sold	short tons	128,388	152,412	148,802	r147,584	104,840
Value	thousands	$ 37,888	$ 37,673	$ 43,574	r$ 48,672	$ 46,274
Exports	short tons	r3,884	r4,268	r9,888	r9,666	8,787
Value	thousands	r$ 1,661	r$ 1,835	r$ 3,787	r$ 3,466	$ 2,523
Imports for consumption	short tons	r36,496	r47,271	r51,183	r54,215	27,979
Value	thousands	r$ 6,496	r$ 8,529	r$ 12,885	r$ 16,367	$ 9,184

rRevised.
W—Not available.
1—Withheld to avoid disclosing individual company confidential data.
Source: U. S. Bureau of Mines [6].

Table 12 from the Bureau of Mines document [6] lists the U. S. producers of iron oxide pigment. Twenty-one companies reported shipments from 72 plants in 13 States. Pfizer, Inc., and Reichard Coulston, Inc., were the largest producers of both synthetic and natural oxides. Cities Service Company, Columbian Division, was also a leading synthetics producer, while the Prince Manufacturing Company, Delta Color & Supply Company, and Blue Ridge Talc Company, Inc., were significant producers of finished natural pigments. Ten producers accounted for 95 percent of the 1975 sales of all finished pigments.

In addition to being in touch with some of the above processors, Crown is working directly with ferrite manufacturers. These include:

Crucible Magnetics Division, Colt Industries,
Arnold Engineering,
Stackpole Carbon,
Allen-Bradley,
3M Company.

8.3 TECHNOLOGY

Increasing concern about the environment and pollution control regulations has led to development of techniques for regeneration of steel plant wastes. Several processes developed for the recycling of hydrochloric acid from ferrous chloride leach liquors also recover iron oxide as a byproduct or coproduct. A developing market for these oxides has led to modifications of systems in order to produce oxides specifically for the pigment and electronics industries. The Port, Woodall-Duckham, and Keramchemie/Lurgi processes, the Falconbridge fluid-bed hydrolyser process, and the Steel Company of Canada, Ltd's, spray roasting procedures were described in the January and February 1975 issues of the Canadian Mining and Metallurgical Bulletin.

TABLE 12. PRODUCERS OF IRON OXIDE PIGMENTS IN THE UNITED STATES IN 1975

Producer	Mailing Address	Plant Location
[illegible] PIGMENTS:		
Blue Ridge Talc Co., Inc.	P. O. Box 39 Henry, Va. 24102	Henry, Va.
Chemalloy, Co., Inc.	County Line Rd. Ro. 950 Bryn Mawr, Pa. 19107	Bryn Mawr, Pa.
Chemetron Pigments	401 Columbia Ave. Holland, Mich. 49423	Harrington, A. Va.
Cities Service Co., Calsimine Div.	P. O. Box 5373 Akron, Ohio 44313	St. Louis, Mo., Monmouth Junction, N.J., Trenton, N.J.
Combustion Engineering, CE Minerals Div.	901 East 8-th Avenue King of Prussia, Pa. 19406	Camden, N. J.
Delta Color & Supply Co.	1050 East Bay St. Milwaukee, Wisc. 53207	Milwaukee, Wisc.
E. I. duPont de Nemours & Co.	Pigments Dept. Wilmington, Del. 19898	Newark, N. J.
Ferro Corp., Nubone Chemical Div.	700 North Wheeling St. Toledo, Ohio 43605	Toledo, Ohio
Foote Mineral Company	Route 100 Exton, Pa. 19341	Exton, Pa.
Greenback Industries, Inc. Greenback Ferric Div.	Route 2, Box 63 Greenback, Tenn. 37742	Greenback, Tenn.
Hercules Inc., CAEP Dept.	720 Commerce St. Pulaski, Va. 24301	Pulaski, Va.
Hoover Color Corp.	P. O. Box 218 Hiwassee, Va. 24347	Hiwassee, Va.
Indiana General Corp.	P. O. Box 218 Valparaiso, Ind. 46383	Valparaiso, Ind.
Mineral Pigments Corp.	7811 Walkerie Rd. Baltimore, Md. 20705	Baltimore, Md.
New Riverside Ochre Co.	Box 387 Cartersville, Ga. 30120	Cartersville, Ga.

TABLE 12 (cont'd)

Producer	Mailing Address	Plant Location
Pfizer, Inc., Mineral Pigments Div.	235 East 42nd St. New York, N. Y. 10017	Emeryville, Calif., East St. Louis, Ill., Easton, Pa.
Prince Manufacturing Co.	700 Lehigh St. Bowmanstown, Pa. 18030	Quincy, Ill., Bowmanstown, Pa.
Reichard-Coulston, Inc.	15 East 26th St. New York, N. Y. 10010	Bethlehem, Pa.
George B. Smith Chemical Works, Inc.	1 Center St. Maple Park, Ill. 60151	Maple Park, Ill.
Solomon Grinding Service	P. O. Box 1786 Springfield, Ill. 62705	Springfield, Ill.
Sterling Drug Inc., Hilton-Davis Chemicals Div.	2235 Langdon Farm Rd. Cincinnati, Ohio 45237	Cincinnati, Ohio
Sterling Drug Inc., Thommasett Color Div.	720 Lister Ave. Newark, N. J. 07105	Newark, N. J.
CRUDE PIGMENTS:		
The Cleveland-Cliffs Iron Co.	1460 Union Commerce Bldg. Cleveland, Ohio 44115	Ishpeming, Mich.
Hoover Color Corp.	P. O. Box 218 Hiwassee, Va. 24347	Hiwassee, Va.
Bethlehem Steel Corp.	Martin Towers Bethlehem, Pa. 18016	Sullivan, Mo.
Nemaxx Mining Co.		
New Riverside Ochre Co.	Box 387 Cartersville, Ga. 30120	Cartersville, Ga.

SECTION 9

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3. Higgins, I. R., and J. Ferner, "Split Loop Contactor," U. S. Patent No. 3,460,707, 1972.

4. Manche, E. B., "Nitric Acid Pickling," U. S. Patent 2,643,204, 1953.

5. American Public Health Association; American Water Works Association, Water Pollution Control Federation, "Phenanthroline Method," p. 189; "Standard Methods," 1971.

6. Collins, Cynthia T., "Iron Oxide Pigments," Bureau of Mines Yearbook, Vol. I, U. S. Department of the Interior, 1975.